Seasonal and spatial trends in particle number concentrations and size distributions at the children's health study sites in Southern California

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Continuous measurements of particle number (PN), particle mass (PM_{10}) and gaseous copollutants (NO_x, CO and O_3) were obtained at eight sites (urban, suburban and remote) in Southern California during years 2002 and 2003 in support of University of Southern California Children's Health Study. We report the spatial and temporal variation of PNs and size distributions within these sites. Higher average total PN concentrations are found in winter (November to February), compared to summer (July to September) and spring (March to June) in all urban sites. Contribution of local vehicular emissions is most evident in cooler months, whereas effects of long-range transport of particles are enhanced during warmer periods. The particle size profile is most represented by a combination of the spatial effects, for example, sources, atmospheric processes and meteorological conditions prevalent at each location. Afternoon periods in the warmer months are characterized by elevated number concentrations that either coincide or follow a peak in ozone concentrations, suggesting the formation of new particles by photochemistry. Results show no meaningful correlation between PN and mass, indicating that mass based standards may not be effective in controlling ultrafine particles. The study of the impact of the Union worker's strike at port of Long Beach in October 2002 revealed statistically significant increase in PN concentrations in the 60–200 nm range ($P<0.001$), which are indicative of contributions of emissions from the idling ships at the port.
Journal of Exposure Science and Environmental Epidemiology (2006) **16,** 3–18. doi:10.1038/sj.jea.7500432; published online 3 August 2005

Introduction

A number of observational studies have demonstrated acute and chronic effects of ambient particles on human health (Dockery and Pope, 1994; Pope, 2000; Zanobetti et al., 2000). To this date, however, there appears to be heterogeneity in particulate matter (PM) concentrations and PM-associated health effects between locations within an urban setting, which raises considerable uncertainties as to whether PM mass, number, size, bulk or surface chemistry are the appropriate metrics associated with PM toxicity. For example, recent studies have shown that atmospheric ultrafine particles (with physical diameter <100 nm) have the potential for eliciting adverse health effect (Oberdörster and Utell, 2002; Li et al., 2003, 2004; Xia et al., 2004). Recent epidemiological studies by Peters et al. (1997) have demonstrated a higher association between health effects and exposures to ultrafine particles compared to accumulation mode or coarse particles.

In the complex environment of an urban atmosphere, there is great variability in the number and type of sources of particles as well as in the diurnal and seasonal patterns of their emission strengths, all of which affect human exposure. As one of many sources contributing to urban air pollution in general, the combustion of fossil fuel in motor vehicles is one of the major primary emission sources of ultrafine particles in urban atmospheres, especially in the developed nations (Shi et al., 1999; Cyrys et al., 2003). Recent studies have shown a dramatic decrease of ultrafine number concentrations with increasing distance from busy freeways in Los Angeles, thereby demonstrating that vehicular pollution is a major source of ultrafine particles and that high number concentrations can be a localized phenomenon, on scales of 100–300 m (Zhu et al., 2002a, b). In addition to their direct emission in the atmosphere, particles may be formed as a result of photochemical reactions from gaseous precursors, including particulate sulfate formed from precursor sulfur dioxide, and secondary organic aerosols, formed from oxidation of aromatic hydrocarbons (Derwent et al., 2000). The secondary aerosol formation is largely governed by meteorological factors (Mäkelä et al., 1997; Kim et al., 2002). The high degree of temporal variability of the meteorological parameters such as degree of solar radiation, atmospheric mixing depth, humidity and temperature — all contribute to the temporal variation in particulate number concentrations at a location.

Understanding how the number concentrations of particles change as a function of particle size, time of the day, location and season may help characterize the sources of these emissions as well as refine human exposure parameters used in epidemiological studies that attempt to link particulate levels and health effects they induce.

Due to recent health concerns, particle size distributions and number concentrations in several cities have been measured. Some recent continental sampling campaigns that measured size distributions include the Pittsburgh Air Quality Study (Stanier et al., 2004), the Atlanta PM Supersite program (Woo et al., 2001), and sampling campaigns in Los Angeles (Kim et al., 2002; Fine et al., 2004), Northern Europe (Ruuskanen et al., 2001), Tennessee (Cheng and Tanner, 2002), Brisbane, Australia (Morawska et al., 2002), the UK (Harrison et al., 2000), Estonia and Finland (Kikas et al., 1996) and Central Europe (Birmili et al., 2001). Most of these studies were con ducted in urban areas in which the vast majority of ultrafine PM originate from primary sources (Morawska et al., 1998; Harrison et al., 2000; Woo et al., 2001), thus their diurnal profiles match those of local vehicular sources. The majority of these studies were also intensive in nature, conducted for a period ranging from a few weeks to a few months.

Shi et al. (2001) measured temporally resolved number concentrations to examine periods of nucleation events. Lawless et al. (2001) used the near continuous data obtained from a Scanning Mobility Particle Sizer and an optical particle counter to distinguish between primary and secondary contributions to $PM_{2.5}$ in Fresno, CA. These studies were intensive in nature, focusing on one specific location and for a limited time period. The spatial aerosol characteristics at different locations of a city have also been examined. Kim et al. (2002) identified periods of photochemistry and long-range advection as sources of ultrafine PM at two sites in Los Angeles Basin in addition to local vehicular emissions. Fine et al. (2004) inferred sources of ultrafine particles at two different locations in the eastern portion of Los Angeles Basin. Buzorius et al. (1999) measured aerosol characteristics at a series of sites in Helsinki, Finland in order to investigate the transport of aerosol traveling from source sites to receptor sites. Ruuskanen et al. (2001) conducted monitoring in three different European cities using continuous monitors to describe differences among the sites as well as diurnal variations of particle mass and number concentrations. Little information has been reported on the seasonal patterns of size distributions due to the lack of long-term monitoring. Stanier et al. (2004) measured aerosol size distributions at one location in Pittsburgh for an entire year, providing one of the first data sets in Northern United States from which seasonal patterns can be described.

The work presented in this paper is intended to provide more comprehensive information about spatial, seasonal as well as diurnal variations of atmospheric particle numbers (PNs) and size distributions (14–700 nm) within Southern California. This paper utilizes the data set generated in support of the University of Southern California (USC) Children's Health Study (CHS). The CHS, which began in 1993, is one of the largest investigations of the long-term consequences of air pollution on the respiratory health of children. The main goal of CHS is to identify chronic effects of ambient pollutants in Southern California by performing cross-sectional and longitudinal studies in school children in several communities with varying exposures to particulate matter, ozone and acid vapors. In this paper we present ambient PN characteristics measured at eight sites classified as urban (source and receptor) and remote (suburban/mountainous) sites in Southern California during the years 2002 and 2003. The PN concentration data are supported by gaseous copollutants data to help differentiate (mostly) ultrafine particle sources and formation mechanisms at each site as well as their prevalence over different times of day and different seasons.

Methods

Concentrations of carbon monoxide (CO), ozone (O_3), total nitrogen oxide species (NO_x), mass of particulate matter with aerodynamic diameters less than $10\,\mu m$ (PM_{10}) and total PNs were continuously measured in several locations in Southern California as a part of the University of Southern California Children's Health Study, supported by the South Coast Air Quality Management District (SCAQMD) and the California Air Resources Board (CARB). Size resolved submicrometer PNs (14–700 nm) were measured under an additional contract from the CARB and SCAQMD. Continuous data were collected concurrently throughout the calendar years 2002 and 2003. Eight sites were examined in this study, six within the Los Angeles Basin (LAB): Long Beach, Mira Loma, Upland, Riverside, Lake Arrowhead and USC; and two sites at other areas of Southern California: Alpine and Lancaster (as shown in Figure 1). Selection of the sampling sites, discussed in greater detail by Künzli et al. (2003), was made on the basis of their location within the LAB and the presumed contrasting air quality (hence exposure) regimes in terms of PM and gaseous copollutants, which have differentially affected children's health.

Sampling Sites

Los Angeles is a unique air basin because it epitomizes a distinct air quality problem in terms of particle composition, source mix and meteorology. Unlike other metropolitan areas, the unique morphology and climate of Los Angeles

Figure 1. Locations of sampling sites in Southern California.

create major differences in PM characteristics and composition within the basin. During the past 20 years, growth in both the population and the density of emission sources has been greatest in the central and eastern portions of the LAB. Nevertheless, primary emissions of VOC, NO_x and PM are still dominated by the western, or coastal, portion of the region, which contains the greatest concentration of both mobile and stationary emission sources. Overall the highest ambient concentrations occur in the coastal areas for primary pollutants such as CO and NO_2, and in downwind inland valleys for secondary pollutants such as ozone and fine particulate matter. Thus, it remains appropriate to view the western/coastal portion of the LAB as a source region and the inland valleys of the central and eastern basin as receptor areas.

The winter period in the LAB is characterized by surface temperature inversions in the coastal region and generally weak on-shore flow. Hence, the highest ambient levels of primary pollutants such as CO and NO_2 are generally observed in the coastal region during the winter months. In contrast, the "summer/fall" period is characterized by strong temperature inversions aloft, and by strong onshore flow and interior-mountain up-slope flow, which together produce rapid transport of primary pollutants from the coastal region to the interior valleys. Combined with high actinic radiation in the summer, these conditions produce elevated concentrations of a wide spectrum of secondary air pollutants, including ozone and fine PM, in the central and eastern areas of the Basin in the summer. In addition, offshore flow under Santa Ana conditions can trap large quantities of pollution over the coastal regions of the LAB. Particles thus undergo transformations as they move along a wind trajectory from "source" to "receptor" sites in the basin. As a result, significant differences occur in the chemical composition and size distribution of PM in the LAB because

of a wide range of sources, meteorological conditions, atmospheric chemistry and temporal factors.

Located near a busy surface street, the Long Beach station is about 0.5 km northeast of freeway I-405 and approximately 1.5 km east of freeway I-710. The Long Beach station is mostly downwind of these two freeways as well as the Long Beach port, which is situated approximately 7 km south of the sampling station. The Upland site is located in a residential area inside a community trailer park about 100 m from San Bernardino road, and is within 2 km (mostly downwind i.e., north-east) of the freeway 210. The Mira Loma site (about 80 km east of downtown Los Angeles) is located in a building on the Jurupa Valley High School campus, directly southeast of the intersection of freeways 60 and 15. It is surrounded by several major warehouse facilities with frequent heavy-duty diesel truck traffic (Na et al., 2004; Sardar et al., 2004) and near several major cattle feeding operations. The sampling location at Riverside is within the Citrus Research Center and Agricultural Experiment Station (CRCAES), a part of the University of California, Riverside. It is about 20 km southeast of the Mira Loma site and is situated upwind of surrounding freeways and major roads (Phuleria et al., 2004). The desert site of Lancaster is located in the office of Mojave desert AQMD and is approximately 2 km away from the nearest freeway 14. The Lake Arrowhead monitoring station is located in the rim of World High School near highway 18, at an elevation of about 1700 m. It is a purely serene mountainous site with very few local emission sources, but heavily impacted by transported, aged air pollutants. The sampling site at USC is located near downtown Los Angeles, just 100 m downwind of freeway 110. The Alpine station is a remote suburban to rural site located approximately 50 km east of downtown San Diego (approximately 200 km south-east of downtown Los Angeles).

Fresh emissions from vehicular and industrial sources primarily make Long Beach a "source" site, which is at a relatively western location in the LAB and has an urban surrounding. USC, also, has an urban surrounding and is considered a "source" site. It represents an urban mix of industrial, vehicular and construction sources. Riverside, Upland and Mira Loma and Lake Arrowhead are designated "receptor" sites, where the aerosol is composed of advected, aged and photochemically processed air mass from the central Los Angeles Area. The time for air masses to transport from source to receptor sites can vary from a few hours to more than a day (Sardar et al., 2004). It should be noted here that the designation of these sites as "receptors" by no means precludes the impact of local traffic sources, as it will be discussed later in this paper.

Instrumentation

The concentrations of CO were measured near-continuously by means of a Thermo Environmental Inc. Model 48C trace level CO monitor. A continuous Chemiluminescence Analyzer (Monitor Labs Model 8840) was used for the measurement of concentrations of NO_x, while O_3 concentrations were monitored using a UV photometer (Dasibi Model 1003 AH). Total PN concentrations (greater than about 10 nm in diameter) were measured continuously by a Condensation Particle Counter (CPC, Model 3022/A, TSI Incorporated, St. Paul, MN, USA) set at a flow rate of $1.5 l min^{-1}$. In addition to the continuous data described above, efforts were made to monitor the number-based particle size distributions in each site for 1–3 months duration during a warmer and a cooler period. Accordingly, three Scanning Mobility Particle Sizers (SMPS, Model 3936, TSI Incorporated, St. Paul, MN, USA) were deployed by rotation at each site during selected time periods, as shown in Table 1, to measure the size distribution of submicrometer aerosols (14–700 nm) using an electrical mobility detection technique. In this configuration, the CPC flow rate was maintained at $0.3 l min^{-1}$ (with the sheath flow of the SMPS set at $3 l min^{-1}$), and size-segregated PN concentrations were recorded. The CPC total count data were excluded for the months when the CPC was in the

Table 1. Sampling periods during which SMPS-CPC configuration was employed at various sampling sites.

Site no	Site name	Sampling periods
1	Long Beach	Nov '02; Aug–Sep '03
2	Mira Loma	Jan–Feb '02; Jun '02
3	UC Riverside	Nov '02; Mar–Apr '02
4	USC	Dec '02–Jan '03; Sep '03
5	Upland	Aug to Oct '03; Nov, '03–Jan '04
6	Alpine	Apr–May '03; Dec '03–Jan '04
7	Lancaster	Jun–Jul '03
8	Lake Arrowhead	Jul–Aug '02

SMPS configuration (Table 1; Figure 2). Continuous PN and gaseous copollutant concentrations were averaged over 1- and 24-h intervals for the subsequent analysis.

Hourly PM_{10} mass concentrations in each site were measured by low temperature Differential Tapered Element Oscillating Microbalance monitors (low temperature TEOM 1400A, R&P Inc., Albany, NY, USA). Jacques et al. (2004) have described the design and performance evaluation of this monitor in greater detail. Briefly, the system consists of a size-selective PM_{10} inlet, followed by a Nafion® dryer that reduces the relative humidity of the sample aerosol to 50% or less. Downstream from the Nafion dryer and ahead of the TEOM sensor is an electrostatic precipitator (ESP) to alternately remove particles from the sample stream or allow the particle laden sample stream to continue to the sensor. The ESP is alternately switched on and off, for equal time periods of about 10 min. Unlike a standard TEOM monitor, which collects samples and reports mass concentration continuously, the differential TEOM monitor only collects mass on the TEOM sample filter during half of the measurement time of the monitor, the period where the ESP is turned off (typically 5 min). During the other half of the operation, the ESP is energized and only the affects of the sampled gases and any evaporation of previously collected sample are measured by the TEOM sample filter. The change in the collection filter mass obtained while collecting particle-free ambient air provides an internal reference, for the mass change sensed while collecting ambient particulate. Thus, the Differential TEOM directly measures ambient PM mass concentrations while accounting for collection artifacts, including loss of semi-volatile aerosols, adsorption of organic vapors and temperature changes. The study by Jacques et al. (2004) showed that the time averaged TEOM PM_{10} mass concentrations agreed within $\pm 10\%$ with those of collocated Federal Reference Methods (FRM).

The Quality Control and Quality Assurance procedures used in the study to assure accurate and unbiased measurements were performed in accordance with Southern California Particle Center and Supersite (SCPCS) Quality Assurance Project Plan (QAPP). The SCPCS QAPP incorporates all of the elements required by the U.S. EPA for air monitoring programs.

Results

The section describing our results is divided into the following parts: seasonal and spatial trends; diurnal trends; relation between PM mass, PM surface area and PM numbers; and Long Beach October 2002 strike analysis. The latter part is an "opportunistic" study focusing on the impact of the union workers strike at the port of Long Beach on air quality.
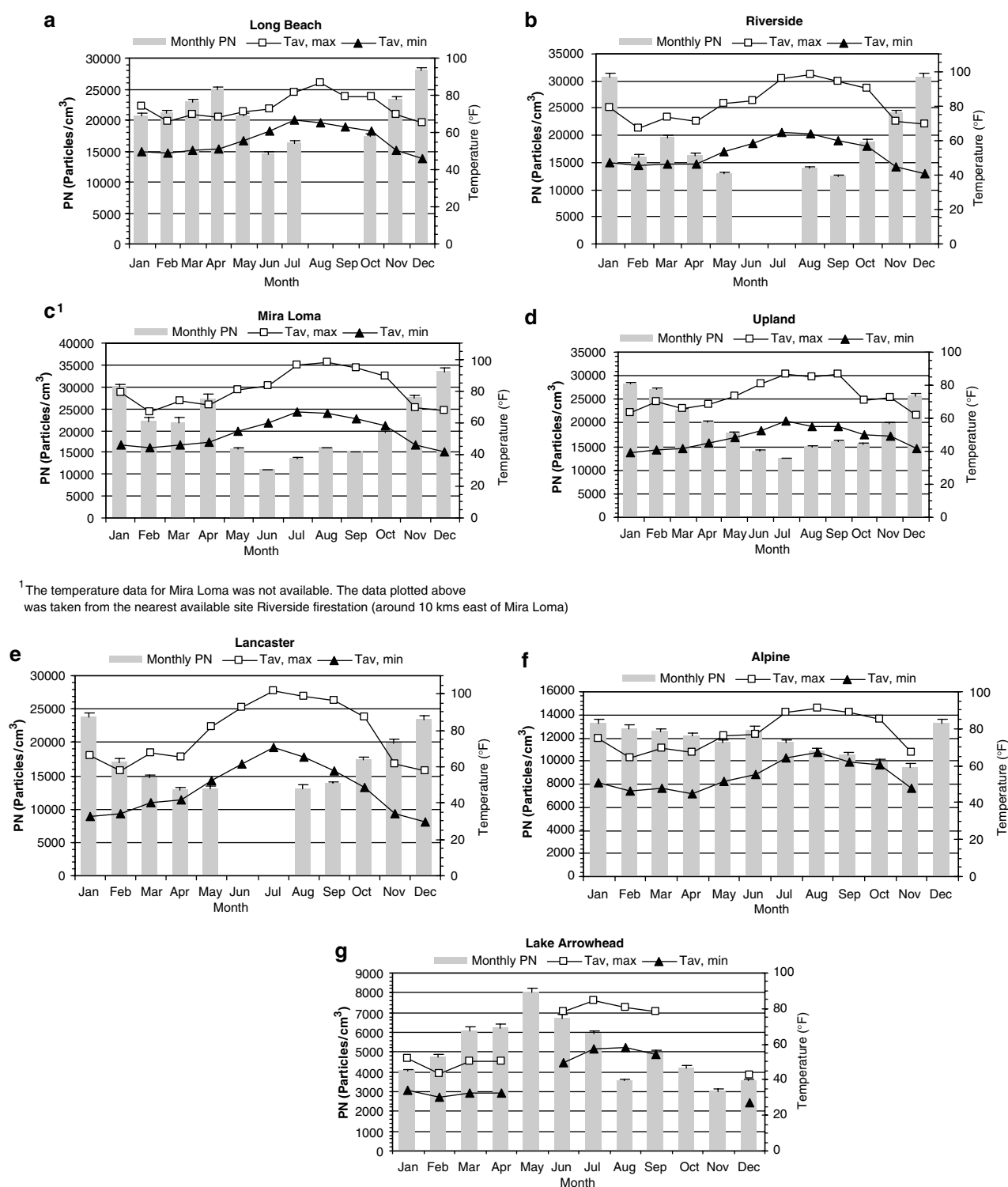
Figure 2. Monthly average particle number concentrations and ambient temperatures at (a) Long Beach, (b) Riverside, (c) Mira Loma, (d) Upland, (e) Lancaster, (f) Alpine and (g) Lake Arrowhead.

[1] The temperature data for Mira Loma was not available. The data plotted above was taken from the nearest available site Riverside firestation (around 10 kms east of Mira Loma)

Seasonal and Spatial Trends

Descriptive statistics (surface area and number median diameter) of the measured particle size distributions are included in Table 2. The number median diameter is defined as the particle diameter that divides the number based frequency distribution of aerosol in half; 50% of the total

Table 2. Summary statistics showing average total particle surface area (SA) and number median diameter (NMD).

Site no	Site name	Season	Period	Particle SA ($\mu m^2/cm^3$)		NMD (nm)	
				Grand avg.	SD	Grand avg.	SD
1	Long Beach	Winter	Nov '02	609.5	320.1	79.9	18.8
	Long Beach	Summer	Aug–Sep '03	330.0	166.0	59.8	18.3
2	Mira Loma	Winter	Jan–Feb '02	674.5	418.5	65.2	19.4
	Mira Loma	Spring	Jun '02	542.9	231.9	81.6	20.5
3	Riverside	Winter	Nov '02	290.3	255.2	47.7	16.6
	Riverside	Spring	Mar–Apr '02	334.0	273.0	62.6	21.3
4	USC	Summer	Sep '03	437.4	331.7	45.9	11.2
	USC	Winter	Dec '02–Jan '03	329.4	210.4	45.4	14.2
5	Upland	Summer[a]	Aug–Sep-Oct '03	371.7	161.9	61.5	14.1
	Upland	Winter	Nov–Dec '03–Jan '04	473.7	300.6	56.6	13.6
6	Alpine	Spring	Apr–May '03	122.4	101.7	42.9	14.4
	Alpine	Winter	Dec '03–Jan '04	135.1	116.5	79.3	18.5
7	Lancaster	Spring	Jun–Jul '03	164.9	136.0	81.9	18.0
8	Lake Arrowhead	Summer	Jul–Aug '02	154.9	117.4	77.9	16.7

[a]Data corresponding to the October Fire in Southern California are excluded.

aerosol number has particles with a larger diameter, and 50% of the total aerosol number has particles with a smaller diameter. Figure 2 shows monthly averaged total PN concentrations measured using the CPC along with the monthly averaged minimum and maximum ambient temperatures, in the eight sites sampled during the calendar year 2003. The error bars indicate the standard error calculated based on the standard deviation of field measurements for each month and the sampling size. A key observation in Figure 2 is the higher average PN concentrations in winter (November to February), compared to summer (July to September) and spring (March to June) in all of the urban sites, for example, USC, Long Beach, Riverside, Upland, Mira Loma and Lancaster. The total PN concentrations at these sites were quite similar and ranged from 25,000 to 30,000 particles/cm^3 in winter months to 12,000 to 15,000 particles/cm^3 in summer/spring months. High number concentrations at the urban sites during winter are likely due to lower temperatures favoring particle formation by condensable organics freshly emitted from vehicles (Shi et al., 1999; Ziemann et al., 2001; Baltensperger et al., 2002).

The lowest levels of PN concentrations were observed at Lake Arrowhead, which is a remote mountainous site. The averaged particle concentrations at this site ranged from 6000 to 8000 particles/cm^3 in summer months and 3000 to 5000 particles/cm^3 in winter months (Figure 2g). The Lake Arrowhead sampling site is located at an elevation of 1700 m. The inversion layer is generally below the station location during morning and evening periods. As the day progresses, the warmer temperature cause the inversion layer to rise and subsequently the inversion layer passes the station elevation and the station is under the inversion layer. During summer months, as a consequence of the elevated mixing height, the site is under the inversion layer for longer periods leading to

higher number concentrations. Additionally, low atmospheric pressure and higher mid-day wind speed during summer favor long-range transport of the aerosol from the much more polluted upwind areas. Biogenic VOC emissions in the Lake Arrowhead region also possibly impact PNs in the summer months.

Particle counts at Alpine, although higher than those observed at Lake Arrowhead, are much lower than those observed in the urban sites, discussed earlier. This site is impacted by very few local traffic emissions and is largely a receptor site of the San Diego metropolitan area. On most summer days, an afternoon peak of particles of possibly secondary origin occurs several hours after the change of wind direction from easterly to westerly. Monthly averaged particle counts range between 9000 and 13,000 particles/cm^3. A detailed discussion about the seasonal variations in particulate characteristics at Alpine is presented in a later section, where size distributions in two separate seasons are discussed.

Figure 3 depicts the particle size distributions measured by the SMPS during different seasons at our sampling sites. Average number size distributions at USC in summer as well as winter are very similar and corroborate the hypothesis that this site is heavily influenced by fresh vehicular emissions. Particles in the 20–50 nm range, which could be attributed to traffic, are the most abundant at this site. Also, number concentrations of this size range increase during the winter period. USC has similar number median diameter during both seasons, an indication of the consistency of the sources (i.e., the traffic emissions from the nearby freeway I-110) affecting PM characteristics in that location.

Similar to USC, at Long Beach, which is also a site highly impacted by vehicular emissions, the average PN concentrations are higher in winter than summer for the
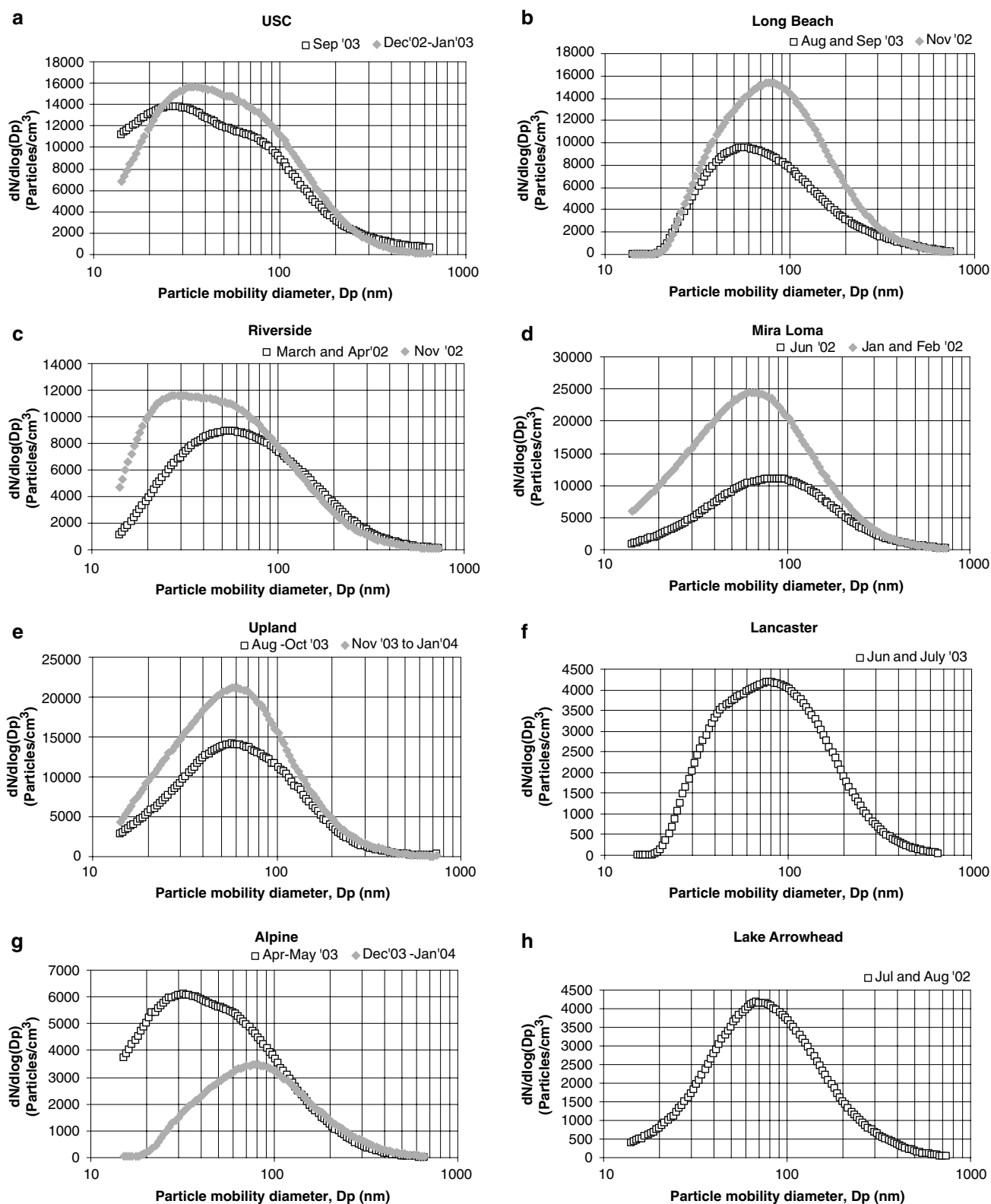
Figure 3. Average number size distributions in winter and summer/spring periods at (a) USC, (b) Long Beach, (c) Riverside, (d) Mira Loma, (e) Upland, (f) Lancaster, (g) Alpine and (h) Lake Arrowhead.

particles >40 nm. However, summer months witness an increase in particles <40 nm diameters. The size distribution in summer supports the hypothesis that this site may be influenced markedly by photochemically generated particles. Given that this site is situated close to the ocean, with the only major upwind sources being the port and the nearby freeway 710, both of which are quite proximal (i.e., within 7 km or less) to the site, the contribution of long range transport to particle numbers can be ruled out. The number median diameter of the aerosol is also lower in summer than in winter. Larger number median diameter in winter (79.9 nm) compared to summer (59.8 nm) may be due to high relative humidity in the winter months, which would contribute to growth of particles by condensation of water vapor in the air. It should be noted that the proximity of that site to the ocean results in unusually higher relative humidity levels compared to the rest of the urban sites, with prolonged periods of night time and morning fog. The smaller summertime number median diameter could be due to the increased photochemical production of smaller particles, as observed by Kim et al. (2002) and Wehner and Wiedensohler (2003). During the first week of October, union workers at the port of Long Beach went on strike. A detailed analysis of the effect of this strike on particulate characteristics of Long Beach is discussed in later section of this paper.

Riverside, Mira Loma and Upland are receptor sites downwind of the high concentration of sources in the western part of LAB. In addition to the effect of few local emission sources, PN concentration at these receptor areas is also influenced by aged, advected aerosol from the west, especially in summer season. The Upland station was directly impacted by Southern California wildfires during late October 2003 because of its location some 3.5 km downwind of one of the 13 fires during that period. The impact of this fire on aerosol characteristics is discussed in detail by Phuleria et al. (2004), and thus we do not present the analysis here. However, for our seasonal characteristics analysis, we have excluded the data from that period.

At Riverside, the PN concentrations are higher in winter compared to spring for particles <100 nm. It is interesting to observe that the particles >100 nm are slightly higher in the spring period. The increase in the peak median size in springtime may be due to the contribution of advected, thus aged aerosols, which are generally larger in diameter (Zhang and Wexler, 2002), from the western polluted regions of the Los Angeles Basin.

The size distribution of aerosols also shows some seasonal variation at Mira Loma. In addition to a decrease in PN concentrations, the number size distribution shifted towards larger sizes in summer compared to winter. Decrease in particle counts of all size ranges in summer reflects the effect of more dilution with elevated mixing height in warmer months. As in Riverside, the number median diameter of the aerosol in Mira Loma is larger in warmer season (Table 2).

This may be the result of the increased wind speeds and onshore flow in the warmer months, leading to increased advection of pollutant air parcels from the western LAB. This advected aerosol is generally larger in diameter as noted earlier and would lead to larger number size distribution of the summer/spring aerosols.

At the suburban remote site Alpine, in contrast to all the receptor sites discussed above, the PNs <100 nm are markedly higher in spring than in winter (Figure 3g). The number median diameter also shifts from 79 nm in winter to 43 nm in spring (Table 2). This may be due to increased summertime advection and photochemical particle formation. The influence of summer advection and photochemical particle formation is supported by wind data, which indicates a change in wind direction from easterly (offshore) to westerly (onshore). The westerly winds would bring the aging air-mass from the San Diego metropolitan area to the station. The afternoon peak of aged and photochemically derived particles occurs several hours after the wind direction change, allowing time for the air mass to reach the station from San Diego.

Particle size distribution data is available for only summer months at Lancaster and Lake Arrowhead. Both sites display generally much lower number concentrations than the urban sites, as one would expect. The relatively large aerosol number median diameter of 82 and 78 nm at Lancaster and Lake Arrowhead, respectively, corroborate the absence of any major local sources, which would emit fresh hence smaller in size emitted PM.
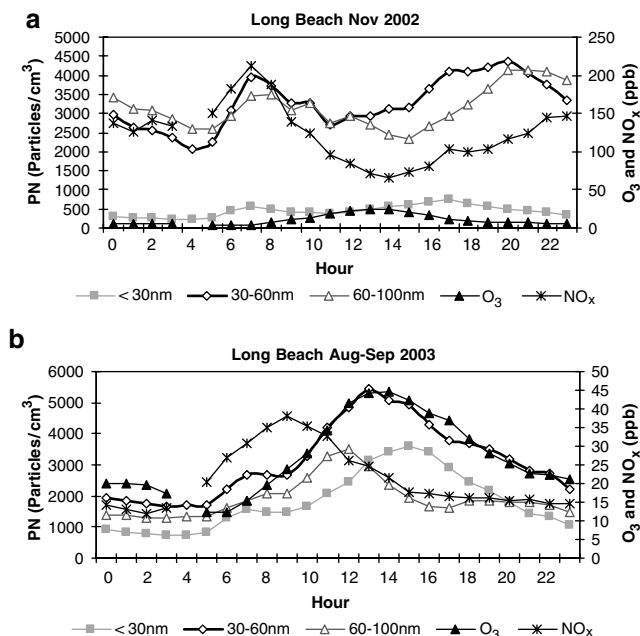
Diurnal Trends

This section describes our observations of diurnal trends in PNs and gaseous copollutants, which, combined with the size distribution and number concentrations data, may provide insights into sources and possible formation mechanisms of particulate matter in each of these sites. Figures 4–9 display the diurnal variations of PN and gaseous pollutants (O_3 and NO_x) concentrations averaged by time of day over the period that SMPS sampled at each of the sites. In these figures, particle sizes have been segregated into three ultrafine size ranges: 15–30, 30–60 and 60–100 nm.

The diurnal trends of PN in different size ranges and gaseous pollutants at USC and Long Beach during the winter sampling periods are shown in Figures 4a and 5a, respectively. As mentioned before, USC and Long Beach are close to vehicular sources and traffic is expected to be primary source of these particles at these sites. The number concentrations have also been observed to be higher during winter months. The diurnal pattern of NO_x is very similar to diurnal patterns of PN concentrations. The morning and evening peaks of these pollutants correspond to morning and evening commutes, which suggests that local traffic is the major contributor to ultrafine PM at both these sites during winter.
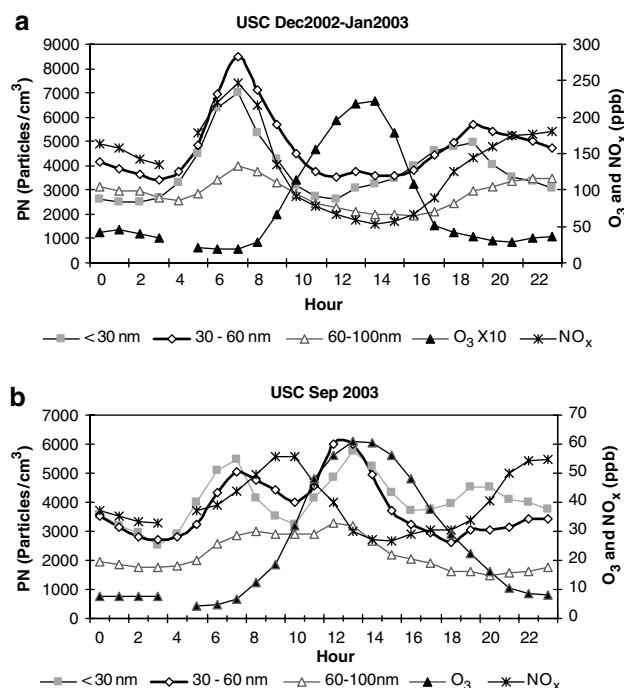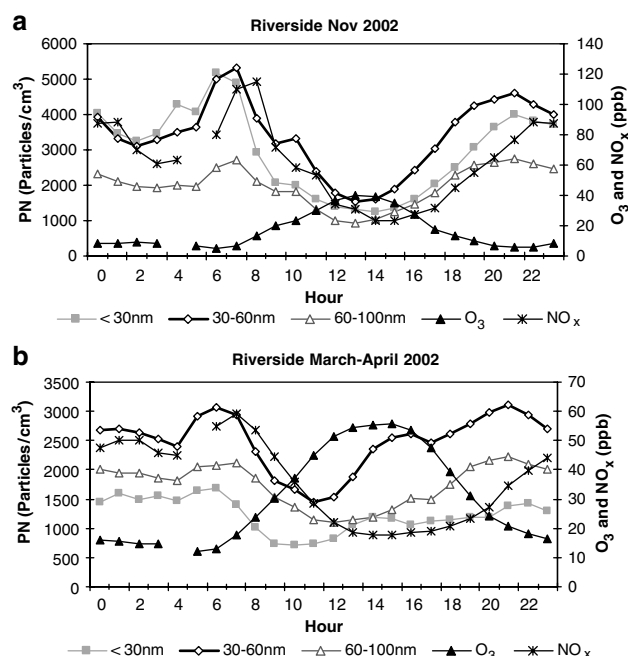
Figure 4. Diurnal trends of size-segregated particle number, O_3 and NO_x at USC during (a) Dec 2002–Jan 2003 and (b) Sep 2003.
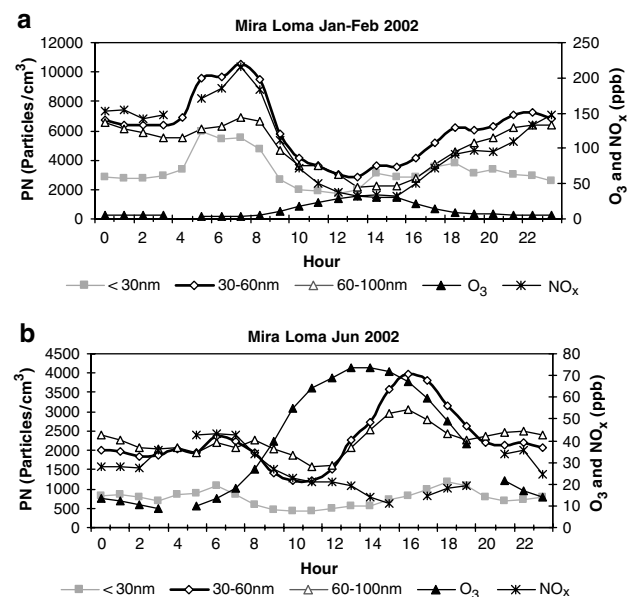

Figure 6. Diurnal trends of size-segregated particle number, O_3 and NO_x at Riverside during (a) Nov 2002 and (b) Mar–Apr 2002.

Figure 5. Diurnal trends of size-segregated particle number, O_3 and NO_x at Long Beach during (a) Nov 2002 and (b) Aug–Sep 2003.

Figure 7. Diurnal trends of size-segregated particle number, O_3 and NO_x at Mira Loma during (a) Jan–Feb 2002 and (b) Jun 2002.

During summer months, secondary aerosol formation is favored and new ultrafine particles may form as a result of the condensation of low-volatility products of photochemical reaction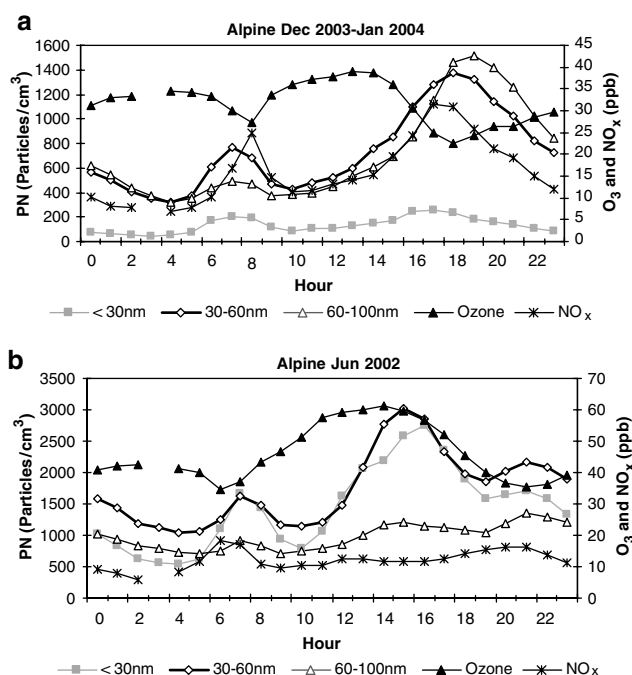s (largely organic compounds) onto stable, nano-meter-size particles (O'Dowd et al., 1999; Kim et al., 2002; Sardar et al., 2004). Secondary aerosol formation is the most likely explanation for the diurnal trends in PN during the summer period at USC and Long Beach (Figures 4b and 5b,

Figure 8. Diurnal trends of size-segregated particle number, O_3 and NO_x at Alpine during (a) Dec 2003–Jan 2004 and (b) Apr–May 2003.
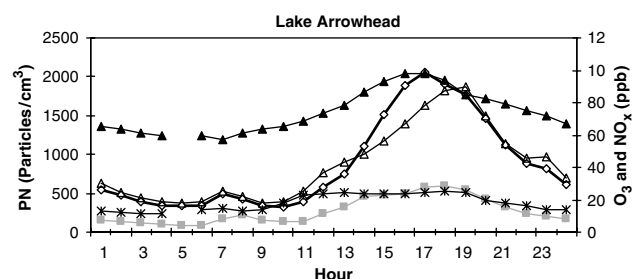
Figure 9. Diurnal trends of size-segregated particle number, O_3 and NO_x at Lake Arrowhead during Jul–Aug 2002.

respectively) in which the peak particle concentrations during the afternoon period either coincide or slightly lag behind the peak in O_3 concentrations.

Figures 6a and 7a show the diurnal trends of PNs as well as gaseous copollutants during winter period at Riverside and Mira Loma, respectively. Similar to the winter diurnal trends of the source sites, we notice a peak in number concentrations in the morning and another smaller peak in the evening across all particle size ranges. The diurnal pattern of NO_x is very similar to diurnal profile of number concentrations at both these sites, indicating once again a traffic origin for these particles during winter. Since PN counts are high and wind speeds are generally low in the morning, the traffic sources are local and specific to the sampling locations. The higher

number concentrations in morning, relative to evening rush hour levels, may be a result of the low mixing height during morning hours. As the day progresses the temperature increases, causing the inversion height to rise. The lower number median diameter of aerosol during winter may also be explained by contribution from fresh emissions in winter. The diurnal patterns of PN concentrations show an additional peak during the afternoon in spring and summer months at Riverside and Mira Loma, respectively (Figures 6b and 7b), similar to those observed during the summer in Long Beach and USC. This peak is either concurrent or slightly lagging the O_3 peak, as in the previous sites. We attribute this increase to secondary aerosol production by photochemical reactions, as discussed earlier, with the lag between the PN and O_3 peaks possibly being due to the time that is required for the newly formed particles to grow to a size that can be detected by the SMPS (i.e., $>15\,nm$).

Similar diurnal patterns of particle counts for winter and summer to the LAB sites are observed at Alpine, depicted in Figure 8. During winter, higher numbers are observed in the morning, when the mixing height of the atmosphere is low. As the day progresses, the temperature increases and mixing height rises, correspondingly the PN concentrations drop due to dilution and dispersion, and they increase again in evening and night when the mixing height depresses. The diurnal trends of particle concentrations also track well those of NO_x. During the warmer period (April and May 2002), the diurnal profile of particulates displays a different trend. There is a surge in PNs in the afternoon, especially for particles below 60 nm, following a very similar pattern to the diurnal profile of O_3, which implies photochemical formation of these particles and air mass advection, as seen at the urban sites discussed earlier.

The diurnal profile of number concentrations and gaseous pollutant concentrations averaged by time of the day over 2 months (July–August 2002) of SMPS sampling in Lake Arrowhead is shown in Figure 9. The diurnal patterns of O_3 and NO_x are very similar to the diurnal patterns of PN concentrations. All pollutant concentrations increase during later part of the day. As discussed earlier, Lake Arrowhead is located at an elevation of approximately 1700 m with negligible local pollution sources. During early morning and night, the inversion layer is generally below the station location. As the day progresses, the warmer temperature cause the inversion layer to rise. Eventually, the station is under the inversion layer. In addition to the contribution of photochemical activity to the total PNs, the rise in PNs during that period is also a result of the increased vertical mixing and advection, which brings to the site aged and more polluted air parcels originating in the western parts of LAB. This is also supported by the unusual rise in NO_x concentrations in the middle of the day, also seen in Figure 9, which cannot be attributed to an increase in traffic or any other factors.

Correlations Between PM Numbers, PM Surface Area and PM Mass

Table 3 presents the Pearson correlation coefficient (R) between total PN concentrations and total surface area concentrations calculated from the SMPS data assuming spherical particles. A moderate to high correlation (i.e., $R = 0.55$–0.90) was observed between PN and surface area concentrations for all sites in both sampling periods. This correlation was somewhat lower in the warmer period for all the sites in this study except Riverside and Long Beach. Strom et al. (2003) also found higher correlations between PN and surface area in winter compared to summer. This finding is consistent with the hypothesis that the increased

aerosol surface area acts as a deposition site for gaseous precursors to condense, thereby preventing new particle formation, as one would expect. The increased surface area may also act as a sink of ultrafine particles via heterogeneous coagulation.

The correlation of hourly and 24-h averaged PM_{10} and PN (PN) concentrations is shown in Table 4 for the different CHS sites. In general, the correlations were found to be weak-to-moderate (i.e., $R < 0.5$), except of the site in Alpine, where relatively strong correlations were observed in the springtime between both the hourly as well as 24-hour averaged concentrations. No particular trend in the hourly or 24-h data between different seasons was observed that could be applied to all sites, as the relationship between the hourly and 24-h PN and PM_{10} varied differentially from site-to-site and within seasons, as evident in the data shown in Table 4.

Long Beach October 2002 Strike Analysis

During the period of 30 September to 9 October 2002, union workers at the port of Long Beach, CA went on strike. The port which is located upwind to the sampling site is considered a major contributor to PM at Long Beach as a result of emissions from ships (Isakson et al., 2003), but perhaps more so because of the heavy-duty truck traffic associated with the port (Chow et al., 1994). It was interesting to determine whether significant changes in particle and copollutant characteristics were observed due to this strike. In order to understand the effects of this strike, we present the PM as well as co pollutant characteristics from pre-, during and poststrike periods in this section. Unfortunately, we do not have the SMPS data from 25 September to 1 October 2002, due to calibration and maintenance performed on the instruments at that time; therefore, PM characteristics for the prestrike period are studied from

Table 3. Pearson correlation coefficient (R) between total particle number concentration and total particle surface area concentration.

Site no	Site name	Season	Period	Pearson correl. coeff.
1	Long Beach	Winter	Nov '02	0.76
	Long Beach	Summer	Aug–Sep '03	0.80
2	Mira Loma	Winter	Jan–Feb '02	0.76
	Mira Loma	Spring	Jun '02	0.53
3	Riverside	Winter	Nov '02	0.69
	Riverside	Spring	Mar–Apr '02	0.69
4	USC	Winter	Dec '02–Jan '03	0.65
	USC	Summer	Sep '03	0.58
5	Upland	Winter	Nov–Dec '03–Jan '04	0.74
	Upland	Summer	Aug–Sep–Oct '03	0.68
6	Alpine	Winter	Dec '03–Jan '04	0.90
	Alpine	Spring	Apr–May '03	0.68
7	Lancaster	Spring	Jun–Jul '03	0.57
8	Lake Arrowhead	Summer	Jul–Aug '02	0.84

Table 4. Correlation coefficient (R) between total particle number concentration and PM_{10}.

Site no	Site	Season	Period	Pearson correl. coeff.	
				Hourly average	Daily average
1	Long Beach	Winter	Nov '02	NA	NA
	Long Beach	Summer	Aug–Sep '03	0.28	0.29
2	Mira Loma	Winter	Feb '02	0.38	0.31
	Mira Loma	Spring	Jun '02	0.29	0.43
3	UC Riverside	Winter	Nov '02	−0.13	0.29
	UC Riverside	Spring	Mar–Apr '02	0.46	0.53
4	USC	Winter	Dec '02–Jan '03	0.14	0.49
	USC	Summer	Sep '03	0.26	0.35
5	Upland	Winter	Nov–Dec '03–Jan '04	0.47	0.20
	Upland	Summer	Aug–Sep–Oct '03	0.19	−0.03
6	Alpine	Winter	Dec '03–Jan '04	0.16	−0.02
	Alpine	Spring	May '03	0.51	0.71
7	Lancaster	Spring	Jun–Jul '03	0.48	0.59
8	Lake Arrowhead	Summer	Jul–Aug '02	0.36	0.26

September 16 to 24, 2002 and for the strike period from 2 to 9 October 2002. Gaseous copollutant data are available throughout the pre-, during- and poststrike periods.

During the strike period, the following three major changes occurred that might have influenced air pollution in that area. First, there was a significant decrease in diesel truck traffic both on the nearby freeways 710 and 110 as well as local surface streets (Figure 10a). Second, about 200 ships were idling off the coast, immediately upwind of the Long Beach throughout the strike period (CNN, 2002). Third, there were significant changes in weather conditions during that period. While in September the weather in Long Beach was warm with the exception of the morning hours, it changed in early October (coincidentally with the strike) to cooler with mostly overcast days (Figure 11c). These weather conditions continued after the strike period. This change may be expected to increase particle concentration by enhancing formation by condensation, but to also particle size condensational growth of the formed particles.

Figure 11a shows the 24-h averaged concentrations of PN and PM_{10} during the strike and nonstrike period. It should be noted here that since the CPC was used in conjunction with the SMPS, the total PNs shown in Figure 11a reflect the sum of the particle counts in each size bin of the SMPS and not those measured by the CPC alone. As other studies have indicated, this may underestimate quite

substantially the total particle concentrations (Liu and Deshler, 2003).

The results of Figure 11a as well as our statistical analysis did not reveal any statistically significant impact of the strike on PN as well as PM_{10} concentrations ($P > 0.05$). The corresponding concentrations of gaseous co pollutants during the strike/nonstrike period are presented in Figure 11b. There is a statistically significant increase in NO_x and CO concentrations during the strike compared to pre- as well as poststrike period ($P < 0.001$). High amounts of NO_x and CO emissions from ships have been observed in previous studies (Corbett and Fischbeck 1997; Cooper, 2003; Sinha et al., 2003; Saxe and Larsen, 2004). These emissions have been reported to be more pronounced when the ships are at berth and idling (Cooper, 2003). We believe that the majority of the increase in CO levels must be attributed to emissions from the idling ships.

Emissions from diesel engines operating in ships contribute significantly to submicrometer range particles and typically have bimodal size distributions, with a dominant mode in the sub-40 nm and a weaker mode in the range of 70 to 100 nm (Isakson et al., 2003). The average size distributions of the PN concentrations before, during and after the strike are shown in Figure 12. Particle concentrations below 60 nm seem virtually unaffected by the strike. Even if a large number of these particles were emitted by ships, it is conceivable that a substantial fraction of them did not reach the sampling station due to coagulation, and/or volatilization processes that may have occurred during their transport. PNs concentrations in the 60–200 nm range were, however, significantly elevated during the strike ($P < 0.001$), which may be indicative of the contributions of emissions from the idling ships. Also, the mode before and after the strike is smaller compared to the strike period, further supporting the argument for the larger-sized particles originating from ship emissions compared to those from heavy and light duty vehicles.

Discussion

PN concentrations and size distributions in complex urban environments can be seen to be highly variable on temporal scales, from diurnal to seasonal, and spatially, from local scale influences, such as distances from highways, to regional scale influences, such as long-range transport across air basins. Seasonal difference in solar intensity, temperature and relative humidity can also strongly influence the diurnal size profile.

This work presents novel data, generated over a 2-year period, related to atmospheric PNs and size distributions (14–700 nm) at eight sites within Southern California generated in support of the University of Southern California Children's Health Study (CHS). The urban site (classified as
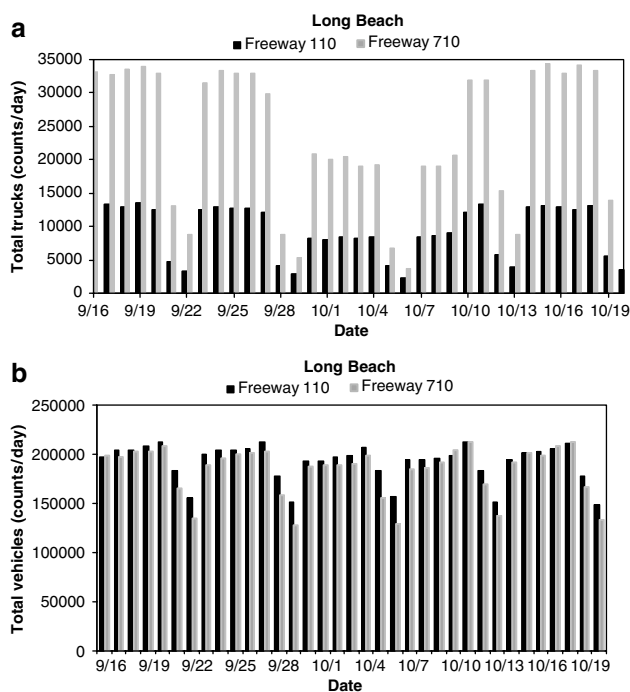
Figure 10. Daily traffic data for Freeways 710 and 410 before, during and after harbor strike at Long Beach in Sep–Oct 2002: (a) total truck counts and (b) total vehicle counts.
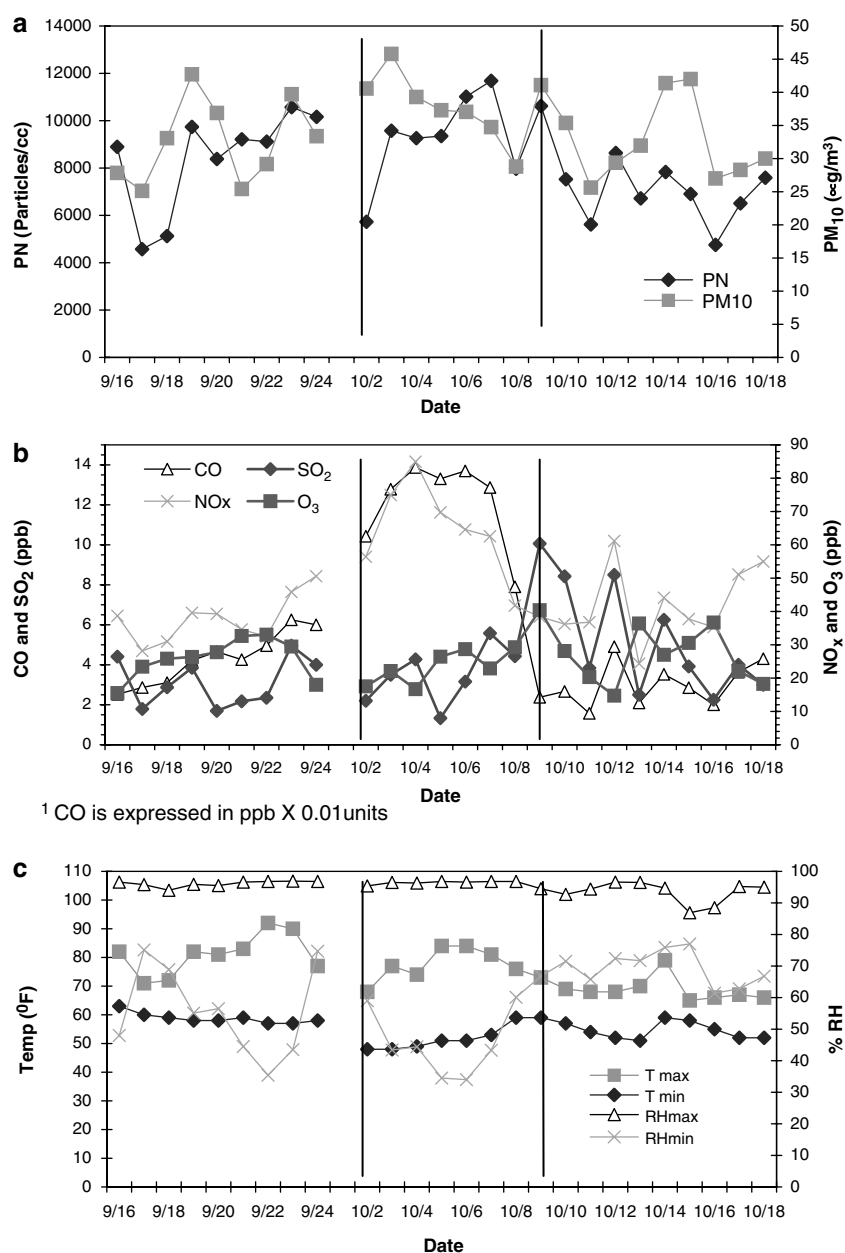
Figure 11. 24-hour averaged (a) PN and PM_{10}, (b) CO, NO_x, and O_3, and (c) temperature and RH — before, during and after the port strike at Long Beach in Sep–Oct 2002.

source and receptor) and remote site (classified as suburban and mountainous) PM size distributions measured during CHS form an excellent data set for research on particle sources and aerosol processes.

In this study we see enhanced contribution of local emission sources during cooler months with stagnant meteorological conditions at all sites. During warmer months, effects of long-range dispersal of aerosol are observed most clearly at the easterly receptor sites of Riverside, Mira Loma and Lake Arrowhead. The increased wind speeds and

onshore flow in the warmer months lead to increased advection of pollutant parcels from the polluted western areas of the LAB (Fine et al., 2004). Additionally, dry and hot summer conditions would limit ultrafine particle growth to accumulation mode during transport (Kim et al., 2002).

In addition to the contribution of vehicular emissions to particle concentrations in Los Angeles, photochemical formation by secondary reactions in the atmosphere appears to be a major source of PM during the afternoon periods in the warmer months at all sites. Current studies by a
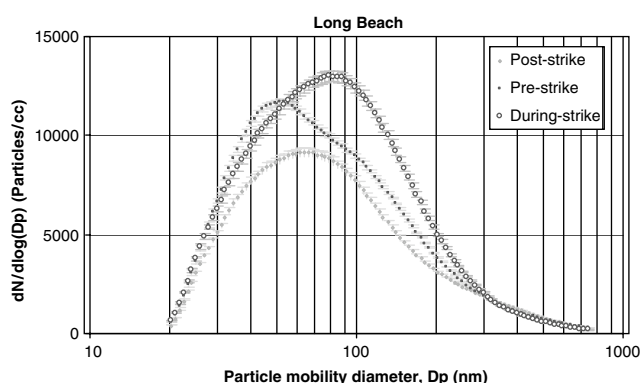
Figure 12. Average particle number size distribution before, during and after the port strike at Long Beach in Sep–Oct 2002.

number of groups have investigated and confirmed the photochemical formation of ultrafine particles in urban atmosphere. In addition to our observations in Los Angeles, secondary particle formation events have been observed in urban areas, including Pittsburgh (Stanier et al., 2004), St. Louis (Shi and Qian, 2003) and Mexico City (Baumgardner et al., 2004). An excellent review of this topic is given by Kulmala et al. (2004). The actual formation mechanism of nanoparticles in the range of 1–3 nm remains largely unknown and has recently become the subject of intensive research in the field of atmospheric science. Current hypotheses on the composition of these fresh nuclei include the binary nucleation of water and sulfuric acid (Kulmala, 2002), ternary nucleation of ammonia–sulfuric acid–water (Weber et al., 1997) and ion-induced nucleation (Yu and Turco, 2001). There is also general consensus that the species responsible for further growth of these nanoparticles to the >10 nm range are different than the nucleating species (Stanier et al., 2004). Our current understanding of atmospheric nanoparticle processes suggests that growth of these particles to larger sizes within the ultrafine PM mode occurs by condensation of low volatility organic species. These species are products of photochemical oxidation of volatile organic precursors on these pre-existing nuclei (O'Dowd et al., 1999; Kulmala et al., 2004). In fact, recent studies by Zhang et al. (2004) showed that nucleation rates of sulfuric acid are greatly increased in the presence of organic acids (including products of atmospheric photochemical reactions), by forming unusually stable organic-sulfuric acid complexes, thereby reducing the nucleation barrier of sulfuric acid.

It is interesting to note in our field measurements that summertime levels of ultrafine particles at source sites, such as long Beach and USC peaked in midday (i.e., noon to 1300), whereas ultrafine PM numbers peak slightly later (i.e., between 1500 and 1600) in the inland receptor sites. A time delay in the peak concentrations observed at the receptor sites is possibly due to the transport time for polluted air masses to reach those sites.

The correlation between PN concentrations and PM_{10} has been widely studied and weak-to-moderate correlations have been generally observed between the two (Morawska et al., 1998; Woo et al., 2001; Noble et al., 2003; Fine et al., 2004; Sardar et al., 2004). Since the fine to ultrafine particle counts are dominated by very small particles and the PM_{10} mass is dominated by fewer, much larger particles, low correlation should be expected, especially in air masses dominated by fresher particles (either primary emission particles or freshly formed secondary particles). In our study, we also found weak-to-moderate correlations between PM_{10} and number concentrations with no particular seasonal trend. These findings are very important from a regulatory perspective because they imply that controlling ambient PM_{10} mass via national air quality standards may not necessarily reduce human exposure to ultrafine particles that dominate the particle counts and have recently been shown to have toxic effects (as discussed in the introductory part of the paper).

In conclusion, the results presented in this paper indicate that location and season significantly influence PN and size distributions in locations within Southern California. Strong diurnal and seasonal patterns in number concentrations are evident as a direct effect of the sources, formation mechanisms, as well as meteorological conditions prevalent at each location during different times of the day and year. These results will be used in the CHS as a first-order indicator of not only human exposure but also inhaled dose to ultrafine PM. They will also be used for the development and validation of predictive models for population exposure assessment to ultrafine PM in complex urban environments, such as that of the Los Angels Basin.

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